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HEAT RESISTANT CHROMATE CONVERSION COATINGS

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by

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Heat Resistant Chromate Conversion Coatings

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ABSTRACT

An investigation of means for preventing the adverse effect of heat on the corrosion resistance of chromated metals was conducted. Treatment of chromated zinc or aluminum by simple immersion in sodium silicate, barium nitrate, glycerine or sodium dichromate solution in some instances provided considerable retention of corrosion resistance in spite of subject on to elevated temperatures up to 200C.

IT IS WELL KNOWN that exposure of chromated (chemical chromate conversion coated) zinc or aluminum to heat can result in a marked decrease in corrosion resistance. Recent studies[1] at this laboratory have shown that the corrosion resistance is adversely affected by temperatures as low as 50C. Heating to 150C or higher has been observed, in some instances, to result in virtually complete loss of salt spray corrosion resistance.

Chromated zinc or aluminum components of military equipment are often necessarily subjected to heat during fabrication, storage, shipment or use. It is, therefore, of interest and importance to develop methods for increasing the resistance of chromated metals to the detrimental effect of heating.

An attempt was made to modify the chromate films in order to impart heat resistance. In order to maintain the simplicity of chromating procedures, modification techniques were mostly limited to simple immersion treatments in room temperature solutions.

EXPERIMENTAL

The solutions initially used to modify the chromate films were sodium silicate, barium nitrate, and glycerin. It was considered that silicate might be adsorbed by or react with the chromate film, thus imparting the heat stability often associated with this material. The reaction of a chromate film with a barium salt solution should result in conversion of soluble chromate in the film to the less soluble barium chromate which might be less detrimentally affected by heat. Application of a film of glycerin might prevent dehydration and the resultant film cracking, and insolubilization of the chromate in the conversion coating.

The preparation of chromated zinc and aluminum is shown in Table I.

While still wet from the water rinse, the chromated metals were immersed into one of the following solutions:

1. 5 ml/l sodium silicate solution (Sp gr 1.38; SiO_2:Na_2O 3.22) for three min; thoroughly water rinsed; drain dried; aged 66 hr.
2. 50 g/l barium nitrate for three min; thoroughly water rinsed; drain dried; aged 66 hr.
3. 100 ml/l glycerin for one min; *no rinse*; drain dried; aged 66 hr.

The treated specimens in triplicate were heated two hr at 100 or 200C, and along with unheated specimens were exposed to five per cent neutral salt spray (Method 811.1 of Fed Test Method Std, No. 151A). The results of the salt spray corrosion tests after 96 hr exposure are shown in Table II.

The immersion treatment of freshly chromated zinc in any of the solutions tested generally improved the corrosion resistance of specimens subjected to heat (see Table II). However, there was slight reduction of the corrosion resistance of unheated specimens as the result of the modifying post treatment with either sodium silicate or barium nitrate solutions.

TABLE I

PREPARATION OF SPECIMENS

Metal	Cleaning	Chromating	Draining and Rinsing
Zinc electroplated from cyanide bath on mild steel panels (10 × 15 cm)	None. Used directly after rinsing	Immersed 20 sec in solution of: Sodium dichromate 200 g/l; Sulfuric acid (sp gr 1.84) 6 ml/l; 25C, pH 0.8	Drained for 5 sec; rinsed in
Aluminum 2024-T3 panels (10 × 15 cm)	Degreased, caustic etched 30 sec at 70C; rinsed; desmutted in 50% by vol. HNO_3 (sp gr 1.42); rinsed	Immersed 5 min in solution* of: Chromic anhydride 5 g/l; Potassium ferricyanide 1 g/l; Barium nitrate 1.9 g/l; Sodium fluosilicate 1.35 g/l; 25C, pH 1.5	flowing water at 25C for 50 sec

*U. S. Pat. 2,796,371, Example A

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TABLE II

CORROSION RESISTANCE OF CHROMATED ZINC AND ALUMINUM MODIFIED BY SOLUTION IMMERSION POST-TREATMENT

Post Treatment	Immersion Time, min	Corrosion Rating* After 96 Hr Salt Spray Exposure (avg of 3)—White Salts					
		Unheated		2 Hr @ 100C		2 Hr @ 200C	
		Zn	Al	Zn	Al	Zn	Al
None	—	5	5	3½	3½	0	1
5 ml/l Sodium Silicate	3	4	5	3	5	2½	2
50 g/l Barium Nitrate	3	4½	5	4	4	3	3½
100 ml/l Glycerin	1	5	5	5	5	3	5

*Corrosion ratings: 5—no corrosion; 4—traces of corrosion; 3—slight corrosion; 2—marked corrosion; 1—considerable corrosion; 0—severe corrosion.

Chromated aluminum, modified by the immersion treatments, and subjected to heating was also superior to unmodified chromated panels (see Table II). The silicate treatment appeared beneficial to specimens heated at only 100C but provided little improvement as a result of heating at 200C. The treatment of chromated aluminum in barium nitrate or glycerin solutions largely prevented the adverse effect of heat on corrosion resistance. The chromate films which were glycerin treated but not rinsed were especially effective, providing complete retention of corrosion resistance although having been heated at 200C. See Fig. 1.

In view of the effectiveness of the glycerin treatment, tests were repeated under the same conditions using ethylene glycol. Ethylene glycol modification of chromated zinc or aluminum was not as effective as the glycerin modification in decreasing the adverse effect of heat on corrosion resistance.

Some limited tests were made to determine the ability of certain metal salts to beneficially modify chromate films. The salts were $Sr(NO_3)_2$, $NiSO_4 \cdot 6H_2O$, $Pb(NO_3)_2$, $Co(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, $Cr_2(SO_4)_3$, $ZnSO_4 \cdot 7H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$, or $Fe(NO_3)_3 \cdot 9H_2O$. They were used at a concentration of 50 g/l with three min immersion at 25C.

A B C D

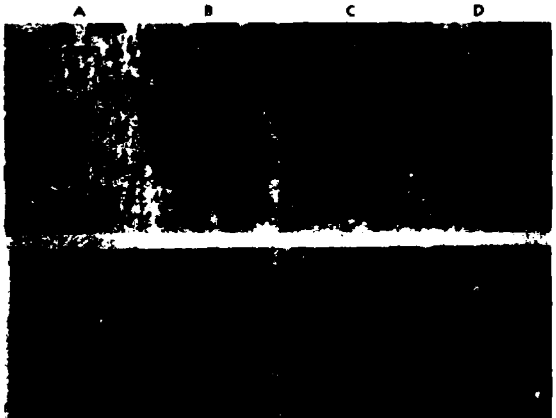

Fig. 1. Chromated specimens, immersion treated, heated two hr at 200C, and exposed to salt spray for 96 hr. Zinc panels at top; aluminum panels at bottom. A. control, B. 180 sec in 5 ml/l waterglass; rinse. C. 180 sec in 50 g/l barium nitrate; rinse. D. 60 sec in 100 ml/l glycerine; no rinse.

None was found superior to the $Ba(NO_3)_2$ treatment described earlier. However, some degree of heat resistance was conferred to chromated aluminum by the strontium, nickel or lead solutions, and to chromated zinc by the strontium, cobalt or aluminum solutions. Further work along these lines is suggested.

Tests were conducted to determine whether dichromate sealed anodized aluminum is adversely affected by heat. Heating for two hr at 200C resulted in crazing of the anodic coating but the corrosion resistance to salt spray was not affected, nor was the amount of leachable hexavalent chromium from the specimens reduced. It was thus considered that similarly dichromate "sealing" of chromate conversion coatings might also provide adsorbed dichromate with immunity to insolubilization of hexavalent chromium by heating.

Immersion of chromated aluminum in 50 g/l $Na_2Cr_2O_7 \cdot 2H_2O$ solution at 95C provided little protection against the detrimental effect of heating. However, when the dichromate concentration was increased to 400 g/l, a one min immersion at 95C did provide chromated aluminum with some resistance to the adverse effect of oven heating at 200C. Such specimens were only slightly corroded after 48 hr salt spray exposure while specimens without dichromate seals were markedly corroded after 24 hr. Dichromate "sealing" of chromated zinc specimens as above caused the chromate films to become quite powdery. The corrosion resistance after heating nevertheless was considerably better than specimens that were not dichromate "sealed."

CONCLUSIONS

Freshly chromated zinc or aluminum may be modified by immersion in sodium silicate, barium nitrate or glycerin solutions at 25C to provide resistance to the adverse effect of heating. Glycerin treatment is particularly effective for chromated aluminum; no loss in corrosion resistance resulted by heating for two hours at 200C.

The corrosion resistance of dichromate sealed anodized aluminum is not adversely affected by two hours' heating at 200C. "Sealing" of chromated aluminum in 400 g/l sodium dichromate at 95C decreases the detrimental effect of subsequent heating on the corrosion resistance.

REFERENCE

1. A. Gallaccio, F. Pearlstein and M. R. D'Ambrosio, *Metal Finishing*, **64**, (8) 50 (1966).

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13. ABSTRACT

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